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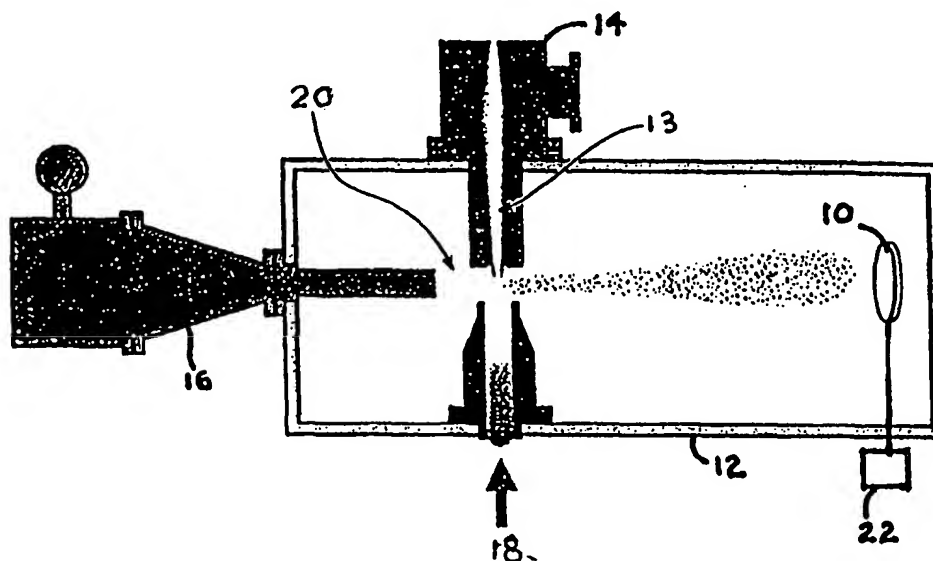
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(54) Title: APPARATUS AND METHOD FOR PRODUCING THERMAL BARRIER COATINGS



(57) Abstract

A method and an apparatus for producing a thermal barrier coating system for a substrate comprising a bond coat adhering to said substrate, a top layer adhering to said bond coat and said top layer having a microstructure comprises at least one zig-zag segment. The method comprises providing said substrate (10) in a deposition chamber (12); impinging an evaporant source (18) with an electron beam (14) to form an evaporant; entraining said evaporant in a carrier gas (20) to form a flow of evaporant; and depositing said evaporant onto said substrate to form said top layer, wherein during the deposition said substrate is rotated by a device (22) so that varying the angle of the incidence of the flow on the substrate.

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Conventionally, the TBC top layer has been produced by one of two processing methods, plasma spray ("PS") or electron beam-physical vapor deposition ("EB-PVD"). Both of these approaches, while useful, suffer from significant disadvantages. Specifically, layers formed using PS systems contain many horizontal pores which result in a low thermal conductivity and, accordingly, good thermal protection properties. However, these disc-like horizontal pores do not contribute to the in-plane compliance and therefore result in poor spallation resistance. Figures 1a and 1b schematically illustrate typical disc-like pores aligned in the plane of a PS coating. These pores impede heat flow through the thickness of the coating, resulting in a coating with a low thermal conductivity. The poor spallation resistance of PS layers results from a combination of the disc-like coating defects and the typically large thermal expansion mismatch between the top coat and bond coat. As a result, PS coatings can be unreliable and tend to be used only to extend component life, not to increase engine operating temperatures.

In contrast, layers formed using EB-PVD possess good spallation resistance, but have poor thermal properties. As schematically illustrated in Figures 2a and 2b, EB-PVD layers have a columnar microstructure featuring columns separated by elongated inter-columnar voids aligned generally perpendicular to the substrate surface. Such a structure results in a low in-plane stiffness, thus reducing thermomechanical stresses during thermal cycling and resulting in an improved spallation resistance compared to that of layers formed using PS systems. However, such a structure fails to sufficiently impede heat flow by conduction or radiation, resulting in a higher thermal conductivity and, accordingly, reduced thermal protection. Efforts to use small (sub micrometer) diameter pores to reduce thermal conductivity have proven unsuccessful because of the high sintering rate of YSZ at the use temperature.

**APPARATUS AND METHOD FOR
PRODUCING THERMAL BARRIER COATINGS**

5 CROSS-REFERENCE TO RELATED PROVISIONAL APPLICATIONS

The present application claims the benefit of the earlier filing date of U.S. Provisional Patent Applications Serial Nos. 60/089,401, filed June 16, 1998, and 60/128,095, filed April 7, 1999, which are incorporated by reference herein in their entireties.

10 STATEMENT CONCERNING FEDERALLY SPONSORED RESEARCH

This invention was made with government support under Grant No. N00014-97-1-0106 awarded by the Office of Naval Research. The U.S. Government has certain rights in this invention.

15 FIELD OF THE INVENTION

The present invention relates to the field of thermal barrier coatings, and more particularly to an apparatus and method for producing functionally graded thermal barrier coatings having a "zig-zag" morphology, and to the thermal barrier coatings produced thereby.

20 BACKGROUND OF THE INVENTION

Thermal barrier coating ("TBC") systems are used for the thermal, oxidation and hot corrosion protection of high-temperature components used in many engineering applications. For example, TBC systems have been important to the development of advanced gas turbine and diesel engines, where they serve to enhance component durability and life and may eventually enable an increase in turbine or engine operating temperatures (and therefore improved engine efficiency).

25 TBC coating systems typically consist of three layers, a thermally insulating top layer, a thermally grown oxide ("TGO") and an underlying bond layer. The top TBC

layer is typically a porous ceramic layer formed from a low thermal conductivity material such as zirconia (ZrO_2), stabilized by yttria (Y_2O_3), ceria (CeO_2), magnesia (MgO), or another oxide. The bond layer or bond coat typically is a metallic, oxidation-resistant material such as platinum aluminide (PtAl) or another aluminide, or MCrAlY , where $\text{M} = \text{Ni}$ or Co . The top TBC layer provides thermal insulation to the underlying component, whereas the bond layer oxidizes prior to or during the deposition of the top layer, or in service, to form the thin TGO layer, which typically consists of α -alumina. The TGO layer improves the adherence of the top layer to the underlying component, and protects the underlying component from oxidation and hot corrosion.

To be effective, a TBC coating system must have a low thermal conductivity to thermally insulate the underlying component from hot engine gases. It must also be compliant in order to minimize stresses that result during thermal cycling because of the different coefficients of thermal expansion of the TBC coating system and the underlying materials. Minimizing such stresses is important, as they will result in cracking and spalling of the TBC coating system, and failure of the underlying component.

It is well-known that the structural performance and thermal properties of TBCs are strongly influenced by the relative amount and orientation of porosity in the top layer. Specifically, in order to achieve high in-plane compliance associated with good structural performance, it is desirable that the top layer have a porous microstructure featuring pores or discontinuities extending through the thickness of the layer, i.e. in a vertical plane, such as with columnar pores. To achieve good thermal properties, however, the top layer preferably will have a microstructure featuring discontinuities or voids which do not extend over the thickness of the layer, but instead extend in a horizontal plane in such a way that the conduction of heat and the propagation of radiant energy are both impeded.

Exceptional structural performance and thermal performance are competing requirements which, until now, have not been satisfactorily reconciled. There is a marked need for coating systems which exhibit exceptional performance on both fronts, particularly given that the future development of advanced turbines and other systems will require TBC coating systems designed to operate at increased temperatures, requiring reduced thermal conductivity and a low in-plane stiffness in the top layer. Although such performance requirements may be achieved with the development of new TBC materials with improved properties, such materials (if capable of being produced at all) will likely be chemically more complex and expensive, and more difficult to deposit than materials currently in use. Thus, new deposition approaches that provide dramatic improvements over conventional TBC systems such as PS and EB-PVD are needed to meet emerging technological advances in turbines, engines and other machines in which TBCs may be used.

Accordingly, it is an object of the present invention to provide a method and apparatus for producing improved TBCs by manipulating column morphology and pore geometry to control the properties of vapor-deposited materials.

It is another object of the present invention to provide a method and apparatus for producing TBCs that are capable of simultaneously providing exceptional structural performance and exceptional thermal performance.

It is yet another object of the present invention to provide a method and apparatus for producing TBCs having thermal performance at least as good as that achievable using conventional PS processing systems, but with markedly improved structural performance over that which may be achieved using conventional PS processing systems.

It is another object of the present invention to provide a method and apparatus for producing TBCs that are capable of meeting the emerging technological advances in

turbines, engines and other machines in which TBCs may be used.

It is still another object of the present invention to provide new TBCs which are capable of meeting the emerging technological advances in turbines, engines and other machines in which TBCs may be used.

5 SUMMARY OF THE INVENTION

The present invention is directed to an apparatus and method for producing TBC coating systems having both exceptional thermal performance and exceptional structural performance. The method of the present invention generally comprises the steps of providing a substrate, providing a source material to be deposited onto the substrate, and depositing the
10 source material onto the substrate for a period of time T_1 and at an angle of incidence θ_1 , where $|\theta_1|$ is less than about 70° . After time period T_1 , the angle of incidence is changed to an angle θ_2 , where $|\theta_2|$ is less than about 70° , and the source material is deposited onto the substrate at angle θ_2 for a period of time T_2 . Preferably, the source material is deposited until a coating thickness greater than about $1 \mu\text{m}$ is achieved. It should be noted that the terms
15 “about” or “approximately,” as used in the present application, are intended to encompass values within $\pm 25\%$ of the stated value.

As a result of the method of the present invention, a coating having a thermally stable (sintering resistant), “zig-zag” shaped microstructure and exceptional structural and thermal properties useful for a TBC is formed. Such a zig-zag microstructure has not
20 heretofore been disclosed for use in producing TBC coating systems. Robbie, et al. disclosed a technique for forming “sculpted” films having helical, square helical or zig-zag type shapes, but the stability of such structures, the processes by which they are formed, and the uses proposed for such structures are far different than those of the present invention. See Robbie, et al., “Sculptured Thin Films and Glancing Angle Deposition: Growth Mechanics and

Applications," J. Vac. Sci. Technol. A., Vol. 15, No. 3, May/June 1997. The Robbie, et al. films are thin films of 60 nm to 1 μ m which are extremely delicate, and therefore require the formation of a planar, dense cap on top of the film. Such films clearly are too fragile for use as TBCs, which are typically in the 10 μ m to 150 μ m thickness range (and preferably are from about 1 μ m to about 150 μ m thick), require a high degree of structural stability, and require a low thermal conductivity to which the use of a dense cap structure would be antithetical. Indeed, the sculpted films formed by Robbie, et al. are not identified as having special structural or thermal properties. Instead, Robbie, et al. suggest using the films formed by their method for optical, chemical or biological devices such as chemical sensors, catalytic reaction surfaces, index gradient materials, anti-reflective coatings, or prosthesis coatings promoting bone attachment. Robbie, et al. also disclose forming their films using an angle of incidence θ greater than 70°, in contrast to the TBC-forming method of the present invention which involves angles of incidence θ less than about 70° and preferably from about 45° to about 60°. It is also apparent that, due to the high angles of incidence employed by Robbie, et al., the deposition rate and materials utilization efficiency ("MUE") of the process would be too low to permit the process to be commercially useful. Thus, Robbie, et al. neither teach nor suggest that, properly deposited, metal and ceramic materials may be used to form zig-zag coatings having exceptional thermal and structural properties useful in TBC coating systems.

The method of the present invention may include depositing a source material directly on a substrate, or depositing the source material as a top layer adhering to a bond coat or other layer adhering to the substrate. Where the latter embodiment is employed, the step of providing a source material comprises providing a substrate having a bond coat or other layer thereon, and the steps of depositing the source material onto the substrate comprise depositing the source material onto the bond coat or other layer. The top layer of deposited source

material has a microstructure comprising at least one zig-zag segment, wherein the top and bond coats act together as a thermal and oxidation protection to the substrate. Where the TBC includes a bond coat for oxidation protection, the bond coat may be formed from any alumina layer forming an oxidation-resistant material, such as, for example, platinum
5 aluminide (PtAl) or another aluminide, or MCrAlY, where M = Ni or Co.

The substrate may be any material on which a TBC would be useful, including components such as a turbine blade, combustor, augmentor or other engine component. The source material may be any material that is useful for forming a TBC on a substrate, including materials such as ZrO_2 , or an oxide-stabilized zirconia such as yttria stabilized zirconia
10 ("YSZ"), ceria stabilized zirconia or magnesia stabilized zirconia. The ability to manipulate thermal conductivity may enable many materials not presently used to form TBC layers to be used for TBC applications in the future.

The resistance of a coating to strain, and thus its ability to resist spallation, may be improved by increasing the porosity or segmentation of the layer. Most preferably,
15 the layer will have a columnar microstructure. Thus, the deposition step of the method of the present invention preferably is performed using a deposition system capable of forming a coating having increased porosity or segmentation, or most preferably, a columnar microstructure. In one embodiment of the method, this is achieved using a physical vapor deposition technique, although other techniques capable of forming such microstructures may
20 also be used to similar advantage.

The step of changing the angle of incidence involves altering the direction of source material deposition flow relative to the substrate, and may comprise using a substrate manipulation device or a flow manipulation device. The substrate or flow manipulation device may comprise manual means, or an electronic motor, electric/magnetic fields and gas

dynamic deflection, or other mechanized means. Where mechanized means are used, such means preferably are computer controlled. Although such a device may be employed for moving the substrate about the substrate's lateral axis, the substrate preferably is held fixed relative to its normal axis during deposition in order to form a more stable microstructure.

5 The steps of depositing the source material onto the substrate for a period of time T_1 and depositing the source material onto the substrate for a period of time T_2 preferably are performed using approximately the same deposition rate, and also may be performed using T_1 approximately equal to T_2 . The deposition rate may be anywhere from about 0.1 to about 100 $\mu\text{m}/\text{min}$, and is preferably about 3 $\mu\text{m}/\text{min}$ or more. In addition, it is
10 preferable, particularly where T_1 is approximately equal to T_2 , that the angle of incidence θ_2 is approximately equal to $-\theta_1$. In any event, $|\theta_2|$ should be less than about 70° , and preferably is in the range of about 45° to about 60° .

 Additional changes to the angle of incidence may be made after deposition at angles of incidence θ_1 and θ_2 . For example, after time period T_2 , the angle of incidence may
15 be changed to θ_3 , and the source material may be deposited onto the substrate for a period of time T_3 . In addition, after time period T_3 , the angle of incidence may be changed to θ_4 , etc., and the source material may be deposited onto the substrate for period of time T_4 , etc. The values of $|\theta_3|$ and $|\theta_4|$, etc., are less than about 70° , and preferably are in the range of about 45° to about 60° . Additional time periods and respective angles of incidence may also be
20 used.

 The deposition step may also include forming a TBC having a columnar microstructure in which columns are generally spaced apart from one another, such that the intercolumnar spaces decrease with the thickness of the coating, i.e. the space between two columns is less at the top surface of the layer than at the bottom surface. Preferably, the

spaces between the columns decrease to zero or near-zero at the top surface of the TBC to reduce the transport of corrosive materials to the underlying materials.

The method of the present invention for forming TBCs may comprise providing an electron beam-directed vapor deposition ("EB-DVD") system having a deposition chamber, the chamber having coupled thereto a carrier gas stream generating means, an electron beam generating means, a substrate and an evaporant source material. The method may further include providing an incidence angle control mechanism capable of altering the angle of incidence of the evaporant source material on the substrate during deposition, and impinging the evaporant source material with the electron beam to generate an evaporant. The evaporant is entrained in the carrier gas stream. An incidence angle control mechanism of the type previously described is used to form an angle of incidence θ_1 between the substrate and the carrier gas stream, and the evaporant is deposited onto the substrate for a period of time T_1 . The incidence angle control mechanism is then used to form an angle of incidence θ_2 between the substrate and the carrier gas stream, and the evaporant is deposited onto the substrate at the angle of incidence θ_2 for a period of time T_2 .

The present invention is further drawn to an apparatus for producing TBCs, the apparatus comprising a deposition chamber having coupled thereto a carrier gas stream generating means, an electron beam generating means, a substrate and an evaporant source material. The apparatus further has an incidence angle control mechanism which is coupled to the deposition chamber and capable of altering the angle of incidence of a flow of the evaporant source material on the substrate during deposition, such that coatings having the zig-zag microstructures of the present invention may be formed.

The electron beam generating means of the apparatus comprises an electron beam gun coupled to the deposition chamber, the electron beam gun being capable of

providing an electron beam in the deposition chamber when the deposition chamber is maintained at low downstream operating pressures, i.e., ranging from about 0.001 Torr or less to about 10 Torr or more. The carrier gas generating means is capable of entraining the source material and directing the source material to the substrate after the electron beam has impinged upon and vaporized the source material. The use of a carrier gas makes possible the deposition of source material at a high rate and with a high MUE and locally oblique angles of atom/molecule impact with the substrate surface. Preferably, the velocity and flux of the gas atoms entering the deposition chamber, the nozzle parameters and/or the operating pressures may be varied significantly, resulting a broad margin of control over the properties of the deposited layer.

The evaporant source material preferably is disposed in a water-cooled crucible. The evaporant source material may be disposed inside the carrier gas generating means, which may be a nozzle surrounding the crucible or other evaporant source material holding device. The carrier gas may be any inert gas, such as He or a mixture of He and one or more gases selected from O₂, N₂, hydrocarbons (e.g., methane and acetylene), silanes, and other non-He inert gases.

The present invention is further directed to a TBC coating system having exceptional thermal and structural properties for protecting a substrate subjected to high temperatures, the coating system including a bond coat adhering to a substrate, and a top layer adhering to the bond coat. The top layer has a microstructure comprising at least one zig-zag segment, wherein the coating system acts as a TBC providing thermal and oxidation protection to the substrate. The TBC coating system of the present invention may be formed according to a process comprising the steps of providing a substrate, providing a source material to be deposited onto the substrate, depositing the source material onto the substrate

for a period of time T_1 and at an angle of incidence θ_1 , $|\theta_1|$ being less than about 70° . The angle of incidence is changed to θ_2 after time period T_1 , $|\theta_2|$ being less than about 70° , and the source material is deposited onto the substrate at angle of incidence θ_2 for a period of time T_2 . Additional time periods and respective angles of incidence may also be used.

5 The foregoing and other objects, features and advantages of the present invention will be apparent from the following detailed description, taken in connection with the accompanying figures, the scope of the invention being set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a is a schematic representation of a typical microstructure in a layer
10 formed using a prior art PS system;

FIG. 1b is an enlarged view of the area circumscribed by line 1b-1b in the schematic representation of FIG. 1a;

FIG. 2a is a schematic representation of a typical microstructure in a layer
formed using a prior art EB-PVD system;

15 FIG. 2b is an enlarged view of the area circumscribed by line 2b-2b in the schematic representation of FIG. 2a;

FIG. 3 is a schematic illustration showing a first angle of incidence θ_1 between the substrate and the flow of source material;

FIG. 4a is a schematic representation of a preferred embodiment of the zig-zag
20 microstructure of the present invention formed using a preferred embodiment of the method of the present invention;

FIG. 4b is an enlarged view of the area circumscribed by line 4b-4b in the schematic representation of FIG. 4a;

FIG. 5 is a schematic illustration of an EB-DVD system incorporating the

present invention for forming a zig-zag microstructure;

FIG. 6 is a scanning electron microscopy ("SEM") micrograph (700x) showing a TBC layer formed using an EB-DVD system and an angle of incidence $\theta = 90^\circ$;

FIG. 7 is a SEM micrograph (650x) showing a TBC layer formed using an EB-DVD system and an angle of incidence $\theta = 45^\circ$;

FIG. 8 is a SEM micrograph (800x) showing a zig-zag TBC layer formed as described in Example 1;

FIG. 9 is a SEM micrograph (850x) showing a zig-zag TBC layer formed as described in Example 2;

FIG. 10 is a SEM micrograph (850x) showing a zig-zag TBC layer formed as described in Example 3;

FIG. 11 is a SEM micrograph (1000x) showing a zig-zag TBC layer formed as described in Example 4; and

FIG. 12 is a SEM micrograph (850x) showing a zig-zag TBC layer formed as described in Example 5.

DETAILED DESCRIPTION OF THE INVENTION

The preferred embodiments of the TBC forming method and apparatus of the present invention, and the TBCs produced in accordance with the present invention, will now be described in reference to Figures 1-12.

One embodiment of the method of the present invention comprises using a conventional deposition system capable of forming a coating having a columnar microstructure, in connection with a mechanism capable of altering the angle of incidence θ of a flow of source material on a substrate such as a turbine or diesel engine component. The angle of incidence θ is measured, as shown in Figure 3, as the angle between the normal to

the substrate surface and the direction of the flow of source material toward the substrate surface during deposition.

As shown in Figure 3, the deposition process is commenced with the flow F having an angle of incidence $\theta = \theta_1$, and deposition of a source material is continued for a first deposition period T_1 . This results in the growth of a columnar microstructure in which the columns are growing at an angle θ_1' , where $|\theta_1'|$ typically is less than $|\theta_1|$ (i.e., along line G in Figure 3). After the first deposition period T_1 , the substrate is rotated about its axis to a new angle of incidence $\theta = \theta_2$ and vapor is deposited for a second deposition period T_2 . A change in the angle of incidence may be accomplished using an incidence angle control mechanism such as a flow manipulation device capable of changing the direction of flow of the material being deposited, or, alternatively, a substrate manipulation device capable of moving the substrate. For example, where a gas jet is used to entrain the source material and create a flow of such material to the substrate, a flow manipulation device may comprise a flexible jet nozzle made from a flexible tube which is movable by means of a motor or by electric/magnetic fields and gas dynamic deflection. Similarly, a substrate or flow manipulation device may include a computer-controlled, electronic servo-controlled motor or any other type or make of motor capable of rotating the substrate about its lateral axis (e.g., extending out of the page in Figure 3), or altering the direction of flow of evaporant. Both the flow and substrate manipulation devices may be operated manually or automatically.

Deposition at angle of incidence θ_2 typically results in columns growing at an angle θ_2' , where $|\theta_2'|$ typically is less than $|\theta_2|$, and a zig-zag segment is completed. The values of T_1 and T_2 are determined by the deposition rate and the desired length of a zig-zag segment. They preferably range from about 30 seconds to about 5 minutes, with the best structures being formed using values of from about 2.5 to about 5 minutes (using a deposition

rate of about 5 $\mu\text{m}/\text{min}$). Deposition rates may vary from about 0.1 to about 100 $\mu\text{m}/\text{min}$, and typically are from about 5 to about 10 $\mu\text{m}/\text{min}$. The process is stopped once the desired thickness is achieved. For typical TBCs, the desired thickness will range from about 50 μm to 500 μm .

5 Currently, it is a common practice in industry to rotate the substrate about its normal axis N (shown in Figure 3) during deposition in order to achieve columnar microstructures with desirable spallation resistance. We have found, however, that it is preferable to use the method and apparatus of the present invention while holding the substrate fixed relative to its normal axis N during deposition. This ensures a structure
10 having sufficient in-plane compliance to be useful as a TBC, while providing the TBC with exceptional thermal performance.

By repeating several times the process of altering the angle of incidence θ , a zig-zag microstructure of the type schematically illustrated in Figures 4a and 4b may be produced. It is preferable that several additional deposition periods (T_3 , T_4 , T_5 , etc.) are used,
15 along with additional respective angles of incidence (θ_3 , θ_4 , θ_5 , etc.). Ideally, several sets of first and second deposition periods T_1 and T_2 are utilized, using the same deposition rate and with T_1 approximately equal to T_2 and θ_2 approximately equal to $-\theta_1$, and the length of columnar sub-segment S_1 therefore approximately equal to that of columnar sub-segment S_2 , such that a zig-zag microstructure similar to that schematically illustrated in Figures 4a and
20 4b is formed. Such a morphology has been shown to effectively reduce the thermal conductivity of the coating by altering the porosity and the grain boundary orientation, while retaining the columnar structure that is necessary for ideal spallation resistance. The length L of the zig-zag segments produced (as shown in Figure 4a), as well as the lengths of the columnar sub-segments S_1 , S_2 , etc. (as shown in Figure 4b), may be controlled by varying the

deposition rate and/or deposition period.

The inventors hereof have found that deposition at large angles of incidence θ is likely to result in frail structures inadequate for use as TBCs. Accordingly, it is important to ensure that the absolute value of the angles of incidence $|\theta|$ used are less than about 70° .

5 Typically, TBCs having the most preferable thermal and structural properties are formed using angles of incidence $|\theta|$ of from about 45° to about 60° and have thicknesses ranging from about $50\ \mu\text{m}$ to about $500\ \mu\text{m}$.

It is further contemplated under the present invention that zig-zag columnar microstructures may be produced by varying the pressures, flow parameters and/or other
10 variables such that the intercolumnar spacing of the microstructure decreases from the bottom to the top of the TBC formed. The functionally grade structure that is created by this approach can be used to prevent corrosive contaminants from dirty fuels or other substances coming into contact with the TBC coating system from penetrating into the usually porous TBC and damaging the underlying materials. Protecting the TBC coating system from such
15 damage is important, since contamination damage may result in premature spalling or a decrease of the system's thermal properties. Preferably, the intercolumnar spacing is reduced to zero or near-zero at the top surface of the zig-zag layer in order to provide maximum protection to the TBC. It is believed that this will substantially enhance the durability and useful life span of TBCs produced in accordance with the present invention.

20 It will be appreciated by those having skill in the art that the TBC production method and apparatus of the present invention may be used to form a top layer directly on a substrate material, or on a bond coat or other material. Where a bond coat is used, any material known in the art to be useful for TBC applications may be employed, such as a material which is oxidation-resistant at the intended use temperature. For example, in gas

turbine engines, as is known in the art, the bond coat may be made of platinum aluminide (PtAl) or another aluminide, or MCrAlY, where M = Ni or Co.

It also will be appreciated that any conventional TBC or other coating deposition system, and any source material, capable of forming a columnar microstructure and possessing sufficiently low thermal conductivity for use in thermally protecting a substrate may be used for the present invention. For example, the deposition system used may be any form of physical vapor deposition ("PVD") system, and the source material may comprise a single material or multiple materials, such as ZrO₂, YSZ, ceria-stabilized zirconia, magnesia-stabilized zirconia or other oxide-stabilized zirconia or other materials. The source material also may be provided in any form, including, for example, a cooled wire, or a water cooled copper crucible feed system. Similarly, any incidence angle control mechanism may be used, provided that it is capable of altering the incidence angle of the substrate relative to the flow of material being deposited.

In a preferred embodiment of the present invention, an EB-DVD system is employed, such as disclosed in U.S. Patent No. 5,534,314 to Wadley, et al., which is incorporated herein by reference in its entirety. Such a system may be used to form a TBC or other coating having a columnar microstructure. As shown schematically in Figure 5, an EB-DVD system includes a substrate 10 disposed in a deposition chamber 12. Substrate 10 may be fixed in position such that it is partially or fully disposed within deposition chamber 12, and may be configured to be movable further within or without deposition chamber 12. Coupled to deposition chamber 12 are an electron beam gun 14 or other electron beam generating means, a gas jet 16 or other carrier gas stream generating means, and an evaporant source material 18. In the embodiment of Figure 5, deposition chamber 12 typically has an operating pressure of from about 0.001 Torr to about 10 Torr, most preferably about 0.1 Torr

to about 1 Torr. However, the operating pressure may be less than about 0.001 Torr or greater than about 10 Torr. The evaporant source material in this embodiment is YSZ (3-11 wt% Ytria). Electron beam gun 14 operates at a power of about 1.5 KW, and is capable of depositing atoms at enhanced, extremely low energy ideal for the creation of a finely porous microstructure. Such low energies preferably are in the range of about 0.04 eV to about 0.08 eV. Electron beam gun 14 has a high accelerating voltage (greater than about 30 KV) to ensure penetration of the electron beam at high gas pressures.

Gas jet 16 operates at a pressure of about 0.1 to about 10 Torr. The carrier gas must be a gas, or combination of gases, which allows penetration of the electron beam from the electron beam gun to the source material. Preferably, the gas is He or a mixture of He and one or more gases selected from O₂, N₂, hydrocarbons (e.g., methane and acetylene), silanes, and other non-He inert gases.

In the present embodiment of the invention, evaporant source material 18 is impinged with electron beam 13 from electron beam gun 14 to generate a vaporized evaporant or vapor flux, which is entrained in the carrier gas stream 20 generated by gas jet 16. Carrier gas stream 20 may be used to focus the vapor flux toward substrate 10 in order to coat substrate 10 with evaporant source material 18. The step of impinging evaporant source material 18 with electron beam 13 may be performed if desired inside gas jet 16 or other carrier gas generating means. For example, carrier gas stream 20 could flow through a nozzle (not shown) surrounding evaporant source material 18. In the present embodiment, an incidence angle control mechanism comprising a substrate manipulation device 22 is used to rotate substrate 10 and vary the angle of incidence of the flow on substrate 10. Substrate manipulation device 22 preferably includes a vacuum rated motor (not shown). The motor used in the present embodiment is model no. U21-RN, manufactured by Empire Magnetics,

Inc of Rohnert Park, California.

In an EB-DVD system of the type previously described, the gas jet acts to collimate the vapor flux, effectively focusing the vapor into a region comparable (or less) than the size of the substrate, vastly improving the MUE of the deposition process. The collimated flux, when combined with a substrate inclined with respect to the jet flow at an angle of incidence less than about 70° , and preferably from about 45° to about 60° , allows zig-zag columns to grow with a deposition rate comparable to current, commercially employed TBC deposition techniques, making possible the achievement of exceptional thermal performance without sacrificing structural performance or adding cost to the product.

Significant advantages are realized by using an EB-DVD system in combination with a substrate or flow manipulation device to obtain the zig-zag microstructures of the present invention. Among other advantages, EB-DVD systems operate in extremely low vacuum environments, permitting the use of relatively low cost pumps and making possible the deposition of materials much more rapidly than is currently feasible by either traditional e-beam evaporation systems or other low vacuum vapor deposition systems. The use of a low vacuum also permits the use of valuable source materials much more efficiently than is possible with conventional systems. Specifically, the carrier gas stream of an EB-DVD system permits the focusing of a high percentage of evaporant source material onto the substrate (in the range of about 50% to 95% or more), as opposed to the low MUE (in the range of about 1% to 10%) achieved by typical EB-PVD systems. The substantially improved MUE possible with EB-DVD systems results in deposition rates in the range of about $5 \mu\text{m}/\text{min}$ to about $50 \mu\text{m}/\text{min}$ or more, which is a significant improvement over the $5 \mu\text{m}/\text{min}$ to $15 \mu\text{m}/\text{min}$ rates achievable using conventional PVD systems. In addition, the low vacuum capability of EB-DVD systems allows such systems to be brought to a suitable

pressure in less than 5 minutes, in contrast to the hours-long pump-down times required by prior art systems. This makes possible the changing of source, substrate, or other system components during maintenance or system reconfiguration shutdowns.

EB-DVD systems advantageously are also more compact than other systems, because they are capable of directed deposition on any desired substrate in any position. Accordingly, they do not require a large evaporant source-to-substrate separation distance. In contrast, line-of-sight deposition systems are inherently less compact due to difficulties in avoiding overheating of the substrate during deposition, resulting in undesirably large source-to-substrate distance requirements. Accordingly, EB-DVD systems permit the coating of single turbine blades and other components sequentially, without a need to employ complicated multi-substrate manipulation systems such as those used by prior systems in order to capture as much evaporant as possible.

Example 1

Three TBC samples were prepared for comparison using an EB-DVD system operating with similar processing parameters, but only one using the zig-zag method of the present invention. To prepare a first sample, YSZ (7 wt% Ytria) was deposited on an IN 100 substrate with a NiAl bond coat. The substrate was maintained at about 1000°C during deposition. A chamber pressure of about 0.35 Torr and an upstream gas pressure of about 2.36 Torr were employed. The gas used was approximately 98.8% He and 1.2% O₂, flowing at about 8.1 standard liters/minute and a speed of about Mach 1.75. Evaporation was begun using an electron beam power of about 1.5 KW. The power was increased in approximately 0.3 KW increments every 2.5 minutes for a total deposition time of about 10 minutes, ending with a maximum power of about 2.4 KW. This was done in an effort to compensate for the changing source material shape during deposition and maintain a generally constant source

material evaporation rate. The TBC was deposited at a rate of about 10 $\mu\text{m}/\text{min}$ at an angle of incidence of $\theta = 90^\circ$. This resulted in a layer having the columnar structure shown in Figure 6, and a thermal conductivity of about 1.5 W/mK at 300° K. The thermal conductivity was measured using a steady-state measurement technique designed to accurately determine the thermal properties of thin (about 140 μm or less) coatings with unique microstructures. The approach involves using an infrared microscope to measure differences on small, millimeter sized specimens. During measurement, heat is applied to the outer surface of the coating using a 10 W continuous-beam laser. The infrared microscope is then used to measure the temperature at different locations along the cross-section of the coating. The thermal conductivity of the coating is determined using the Fourier conduction equation

$$Q = -\lambda A(dT/dx)$$

where Q is the input heat flux, A is the cross-sectional area that the heat flows through, and dT/dx is the temperature gradient over the distance that heat flow is measured. The use of such a steady-state measurement technique is necessary for the accurate measurement of TBC layers with unique microstructures (such as the zig-zag morphology of the layers of the present invention), because conventional transient approaches (e.g., laser flash which directly measures thermal diffusivity) severely stretch the fundamental assumptions used to relate thermal diffusivity to thermal conductivity when nonisotropic porosity exists.

A second sample was prepared by depositing YSZ (7 wt% Yttria) on an IN 100 substrate with a NiAl bond coat. The substrate was maintained at about 1000°C. A chamber pressure of about 0.65 Torr and an upstream gas pressure of about 3.90 Torr were employed. The gas used was approximately 98.7% He and 1.3% O₂, flowing at about 15.2 standard liters/minute and a speed of about Mach 1.75. Evaporation was begun using an electron beam power of about 1.5 KW. The power was increased in approximately 0.3 KW

increments every 5.0 minutes for a total deposition time of about 20 minutes, ending with a maximum power of about 2.4 KW. The TBC was deposited at a rate of about $5 \mu\text{m}/\text{min}$ at an angle of incidence of $\theta = 45^\circ$. This resulted in a layer having the columnar structure shown in Figure 7, and a thermal conductivity of about 1.4 W/mK at 300°K , measured using the steady-state measurement technique described above.

A third sample was made using the same materials and parameters as the second sample, but with a chamber pressure of about 0.65 Torr and an upstream gas pressure of about 3.86 Torr. A first angle of incidence $\theta_1 = 45^\circ$ for a first deposition period $T_1 = 150$ seconds, and a second angle of incidence $\theta_2 = -45^\circ$ for a second deposition period $T_2 = 150$ seconds were employed. The angle of incidence was changed using a substrate manipulation device comprising a computer-controlled electronic motor to rotate the substrate about its lateral axis. The flow of evaporant was not interrupted while the angle of incidence was changed. First and second deposition periods T_1 and T_2 were repeated using first and second angles of incidence θ_1 and θ_2 , respectively, several times. The result was a layer having the columnar zig-zag microstructure shown in Figure 8, and a thermal conductivity of about 1.0 W/mK at 300°K , measured using the steady-state measurement technique described above.

Example 2

A sample was prepared by depositing YSZ (7 wt% Yttria) on an IN 100 substrate with a NiAl bond coat. The substrate was maintained at about 1030°C . A chamber pressure of about 0.19 Torr and an upstream gas pressure of about 1.91 Torr were employed. The gas used was approximately 96.6% He and 3.4% O_2 , flowing at about 7.25 standard liters/minute. An average electron beam power of about 1.29 KW was used, with the power being increased during deposition in an effort to compensate for the changing source material shape and maintain a generally constant source material evaporation rate. The TBC was

deposited at a rate of about $3 \mu\text{m}/\text{min}$ at a first angle of incidence $\theta_1 = 50^\circ$ for a first deposition period $T_1 = 75$ seconds, and a second angle of incidence $\theta_2 = -50^\circ$ for a second deposition period $T_2 = 75$ seconds. The angle of incidence was changed using a substrate manipulation device comprising a computer-controlled electronic motor to rotate the substrate about its lateral axis. The flow of evaporant was not interrupted while the angle of incidence was changed. First and second deposition periods T_1 and T_2 were repeated using first and second angles of incidence θ_1 and θ_2 , respectively, several times. The result was a layer having the columnar zig-zag microstructure shown in Figure 9, and a thermal conductivity of about 1.4 W/mK at 300° K , measured using the steady-state measurement technique described in connection with Example 1.

Example 3

A sample was prepared using the same material and parameters as the sample described in Example 2, except that deposition at the first angle of incidence $\theta_1 = 50^\circ$ was performed for a first deposition period $T_1 = 37.5$ seconds, and a second angle of incidence $\theta_2 = -50^\circ$ for a second deposition period $T_2 = 37.5$ seconds. First and second deposition periods T_1 and T_2 were repeated using first and second angles of incidence θ_1 and θ_2 , respectively, several times. The result was a layer having the columnar zig-zag microstructure shown in Figure 10, and a thermal conductivity less than that achieved in the sample of Example 2.

Example 4

A sample was prepared using the same material and parameters as the sample of Examples 2 and 3, except that deposition at the first angle of incidence $\theta_1 = 50^\circ$ was performed for a first deposition period $T_1 = 150$ seconds, and a second angle of incidence $\theta_2 = -50^\circ$ for a second deposition period $T_2 = 150$ seconds. First and second deposition periods T_1

and T_2 were repeated using first and second angles of incidence θ_1 and θ_2 , respectively, several times. The result was a layer having the columnar zig-zag microstructure shown in Figure 11, and a thermal conductivity less than that achieved in the samples of Examples 2 and 3.

Example 5

A sample was prepared using the same material and parameters as the sample of Examples 2, 3 and 4, except that deposition at the first angle of incidence $\theta_1 = 50^\circ$ was performed for a first deposition period $T_1 = 300$ seconds, and a second angle of incidence $\theta_2 = -50^\circ$ for a second deposition period $T_2 = 300$ seconds. First and second deposition periods T_1 and T_2 were repeated using first and second angles of incidence θ_1 and θ_2 , respectively, several times. The result was a layer having the columnar zig-zag microstructure shown in Figure 12, and a thermal conductivity less than that achieved in the samples of Examples 2, 3 and 4. Given the porous structure of this sample, TBCs formed using the parameters set forth in this example would be expected to be highly compliant and resistant to sintering in high-temperature applications. This should also be true of the zig-zag samples of Examples 1 through 4.

It is believed that the many advantages of the present invention will now be apparent to those skilled in the art. It will also be apparent that a number of variations and modifications may be made thereto without departing from its spirit and scope. Accordingly, the foregoing description is to be construed as illustrative only, rather than limiting. The present invention is limited only by the scope of the following claims.

What is claimed is:

- 1 1. A method for producing thermal barrier coating systems, said method comprising:
2 providing a substrate;
3 providing a source material;
4 depositing said source material onto said substrate for a period of time T_1 and at an
5 angle of incidence θ_1 , said angle of incidence θ_1 being less than about 70° ;
6 changing said angle of incidence to θ_2 after said time period T_1 , said angle of
7 incidence θ_2 being less than about 70° ; and
8 depositing said source material onto said substrate at said angle θ_2 for a period of time
9 T_2 .
- 1 2. The method of claim 1, wherein said step of providing a source material comprises
2 providing a substrate having a bond coat thereon, and said steps of depositing said source
3 material onto said substrate comprise depositing said source material onto said bond coat.
- 1 3. The method of claim 1, wherein said substrate has a normal axis, and said substrate is
2 held fixed relative to said normal axis of said substrate during said steps of depositing said
3 source material onto said substrate.
- 1 4. The method of claim 1, wherein said steps of depositing said source material onto said
2 substrate comprise using a physical vapor deposition technique.

1 5. The method of claim 1, wherein said step of providing a source material comprises
2 providing an oxide-stabilized zirconia.

1 6. The method of claim 1, wherein said step of providing a substrate comprises
2 providing an engine component.

1 7. The method of claim 1, wherein said step of changing said angle of incidence
2 comprises using a substrate manipulation device.

1 8. The method of claim 7, wherein said step of changing said angle of incidence using a
2 substrate manipulation device comprises using an electronic motor.

1 9. The method of claim 1, wherein said step of changing said angle of incidence
2 comprises using a flow manipulation device.

1 10. The method of claim 9, wherein said step of changing said angle of incidence using a
2 flow manipulation device comprises using electric/magnetic fields.

1 11. The method of claim 1, wherein said step of depositing said source material onto said
2 substrate for a period of time T_1 is performed using a first deposition rate and said step of
3 depositing said source material onto said substrate for a period of time T_2 is performed using
4 a second deposition rate, said first deposition rate being approximately equal to said second
5 deposition rate.

1 18. The method of claim 17, wherein said steps of depositing said source material onto
2 said substrate comprise forming a thermal barrier coating having a thickness and a columnar
3 microstructure, said columnar microstructure having columns generally spaced apart from
4 one another, said spaces between said columns decreasing with said thickness of said thermal
5 barrier coating.

1 19. The method of claim 18, wherein said thermal barrier coating has a top surface and
2 said deposition step further comprises decreasing said spaces between said columns to near-
3 zero at said top surface of said thermal barrier coating.

1 20. A method for producing thermal barrier coating systems, said method comprising:
2 providing an electron beam-directed vapor deposition system having a deposition
3 chamber, said chamber having coupled thereto a carrier gas stream generating means, an
4 electron beam generating means, a substrate and an evaporant source material;
5 generating a carrier gas stream using said carrier gas stream generating means;
6 impinging said evaporant source material with said electron beam to form an
7 evaporant;
8 entraining said evaporant in said carrier gas stream to form a flow of evaporant;
9 providing an incidence angle control mechanism and using said incidence angle
10 control mechanism to form an angle of incidence θ_1 between said substrate and said flow of
11 evaporant;
12 depositing said evaporant onto said substrate for a period of time T_1 ;
13 using said incidence angle control mechanism to form an angle of incidence θ_2
14 between said substrate and said flow of evaporant; and

1 12. The method of claim 11, wherein said time period T_1 is approximately equal to said
2 time period T_2 .

1 13. The method of claim 12, wherein said angle of incidence θ_2 is approximately equal to
2 $-\theta_1$.

1 14. The method of claim 13, wherein said angle of incidence θ_1 is in the range of about
2 45° to about 60° .

1 15. The method of claim 1, further comprising the steps of:
2 changing said angle of incidence to θ_3 after said time period T_2 , said angle of
3 incidence θ_3 being less than about 70° ; and
4 depositing said source material onto said substrate at said angle θ_3 for a period of time
5 T_3 .

1 16. The method of claim 15, further comprising the steps of:
2 changing said angle of incidence to θ_4 after said time period T_3 , said angle of
3 incidence θ_4 being less than about 70° ; and
4 depositing said source material onto said substrate at said angle θ_4 for a period of time
5 T_4 .

1 17. The method of claim 1, wherein said deposition step is performed using a deposition
2 system capable of producing a coating having a columnar microstructure.

15 depositing said evaporant onto said substrate at said angle of incidence θ_2 using said
16 deposition system for a period of time T_2 .

1 21. The method of claim 20, wherein said steps of using said incidence angle control
2 mechanism to form an angle of incidence comprise using a substrate manipulation device.

1 22. The method of claim 21, wherein said step of depositing said evaporant onto said
2 substrate for a period of time T_1 is performed using a first deposition rate and said step of
3 depositing said evaporant onto said substrate for a period of time T_2 is performed using a
4 second deposition rate, said first deposition rate being approximately equal to said second
5 deposition rate.

1 23. The method of claim 22, wherein said first and second deposition rates are within the
2 range of about 0.1 to about 100 $\mu\text{m}/\text{min}$.

1 24. The method of claim 23, wherein said first and second deposition rates are about
2 3 $\mu\text{m}/\text{min}$.

1 25. The method of claim 21, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and an angle θ_1 and depositing said evaporant onto said
3 substrate for a period of time T_2 and an angle θ_2 are performed using θ_1 approximately equal
4 to
5 $-\theta_2$, θ_1 being in the range of about 45° to about 60° .

1 26. The method of claim 25, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and an angle θ_1 and depositing said evaporant onto said
3 substrate for a period of time T_2 and an angle θ_2 are performed using θ_1 equal to about 45° ,
4 and
5 θ_2 equal to about -45° .

1 27. The method of claim 26, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and depositing said evaporant onto said substrate for a period
3 of time T_2 are performed using T_1 and T_2 equal to about 150 seconds.

1 28. The method of claim 25, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and an angle θ_1 and depositing said evaporant onto said
3 substrate for a period of time T_2 and an angle θ_2 are performed using θ_1 equal to about 50° ,
4 and
5 θ_2 equal to about -50° .

1 29. The method of claim 28, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and depositing said evaporant onto said substrate for a period
3 of time T_2 are performed using T_1 and T_2 equal to about 75 seconds.

1 30. The method of claim 28, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and depositing said evaporant onto said substrate for a period
3 of time T_2 are performed using T_1 and T_2 equal to about 37.5 seconds.

1 31. The method of claim 28, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and depositing said evaporant onto said substrate for a period
3 of time T_2 are performed using T_1 and T_2 equal to about 150 seconds.

1 32. The method of claim 25, wherein said steps of depositing said evaporant onto said
2 substrate for a period of time T_1 and depositing said evaporant onto said substrate for a period
3 of time T_2 are performed using T_1 and T_2 equal to about 300 seconds.

1 33. The method of claim 20, wherein said carrier gas comprises He.

1 34. The method of claim 20, wherein said step of providing an evaporant source material
2 comprises providing YSZ, said YSZ including from 3 to 11 wt% Yttria.

1 35. The method of claim 20, further comprising, prior to said step of impinging said
2 evaporant source material with said electron beam, providing a chamber pressure of 0.65 Torr
3 and an upstream gas pressure of 3.72 Torr.

1 36. The method of claim 20, further comprising, prior to said step of impinging said
2 evaporant source material with said electron beam, providing a chamber pressure of 0.19 Torr
3 and an upstream gas pressure of 1.91 Torr.

1 37. An apparatus for producing thermal barrier coatings, said apparatus comprising:
2 a deposition chamber, said chamber having coupled thereto a carrier gas stream
3 generating means, an electron beam generating means, a substrate and an evaporant source

material; and

an incidence angle control mechanism coupled to said deposition chamber and being capable of altering an angle of incidence of a flow of said evaporant source material on said substrate during deposition, such that thermal barrier coatings having zig-zag microstructures may be formed.

38. The apparatus of claim 37, wherein said incidence angle control mechanism comprises a substrate manipulation device.

39. The apparatus of claim 37, wherein said incidence angle control mechanism comprises a flow manipulation device.

40. The apparatus of claim 37, further comprising:

an electron beam gun coupled to said deposition chamber, said electron beam gun being capable of providing an electron beam in said deposition chamber when said deposition chamber is maintained at an operating pressure ranging from about 0.001 Torr to about 10 Torr; and

said carrier gas generating means being capable of entraining said evaporant source material and directing said evaporant source material to said substrate after said electron beam has impinged said evaporant source material.

41. The apparatus of claim 40, wherein said evaporant source material comprises ZrO_2 .

42. The apparatus of claim 40, wherein said evaporant source material comprises an

oxide-stabilized zirconia from the group consisting of yttria stabilized zirconia, ceria stabilized zirconia or magnesia stabilized zirconia.

43. The apparatus of claim 40, further comprising a water-cooled crucible, said evaporant source material being disposed in said crucible.

44. The apparatus of claim 40, wherein said evaporant source material is disposed inside said carrier gas generating means.

45. The apparatus of claim 40, wherein said carrier gas comprises an inert gas.

46. The apparatus of claim 45, wherein said inert gas comprises a gas selected from the group consisting of He, O₂, N₂, hydrocarbons and silanes.

47. A coating system for protecting a substrate subjected to high temperatures, said coating system comprising:
a bond coat adhering to a substrate;
a top layer adhering to said bond coat; and
said top layer having a microstructure comprising at least one zig-zag segment;
wherein said coating system provides thermal, oxidation and hot corrosion protection to said substrate.

48. The coating system of claim 47, wherein said coating system has a thermal conductivity not greater than about 1 W/mK.

1 49. The coating system of claim 47, said top layer being formed according to a process
2 comprising:

3 providing a substrate;

4 providing a source material;

5 depositing said source material onto said substrate for a period of time T_1 and at an
6 angle of incidence θ_1 , said angle of incidence θ_1 being less than about 70° ;

7 changing said angle of incidence to θ_2 after said time period T_1 , said angle of
8 incidence θ_2 being less than about 70° ; and

9 depositing said source material onto said substrate at said angle θ_2 for a period of time
10 T_2 .

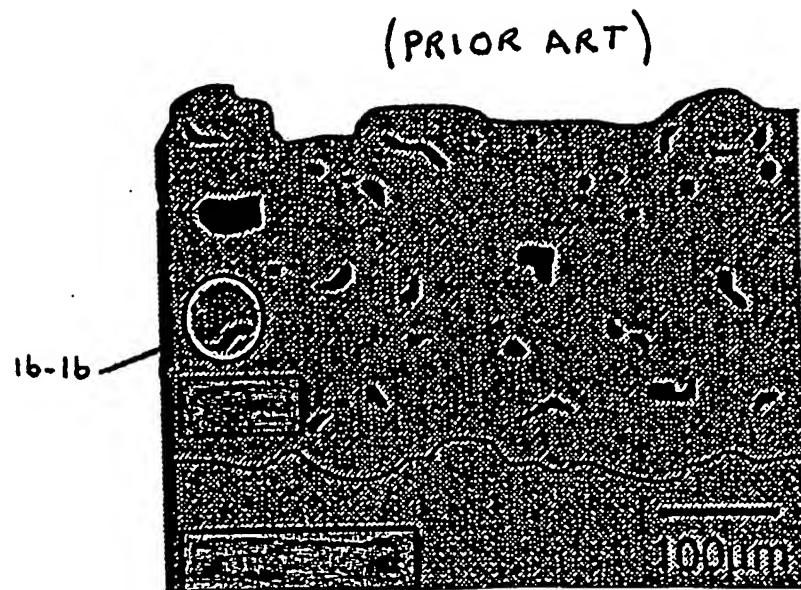


FIG. 1a



FIG. 1b

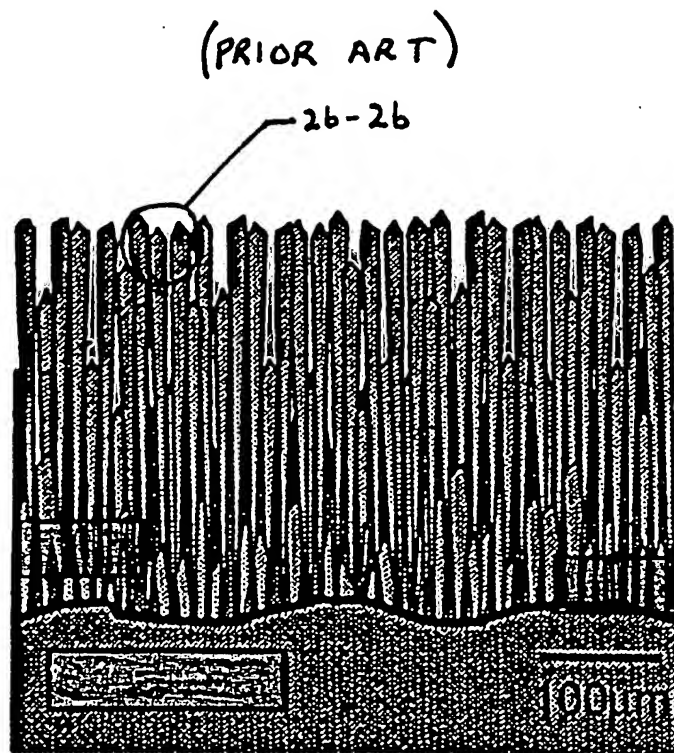


FIG. 2a

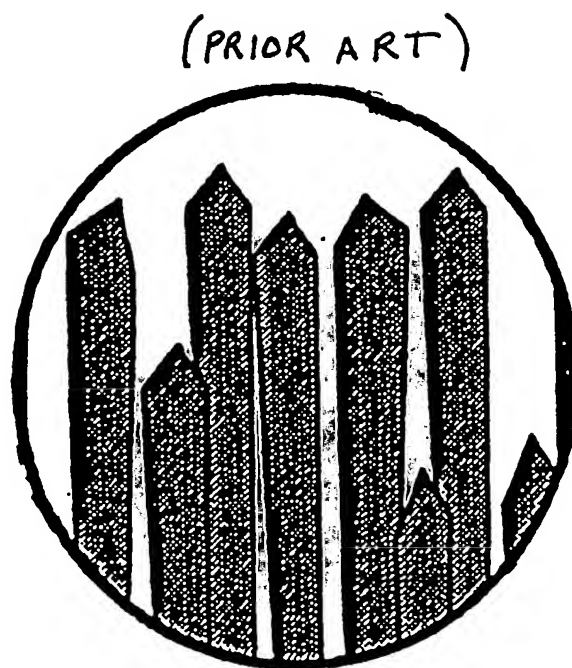


FIG. 2b

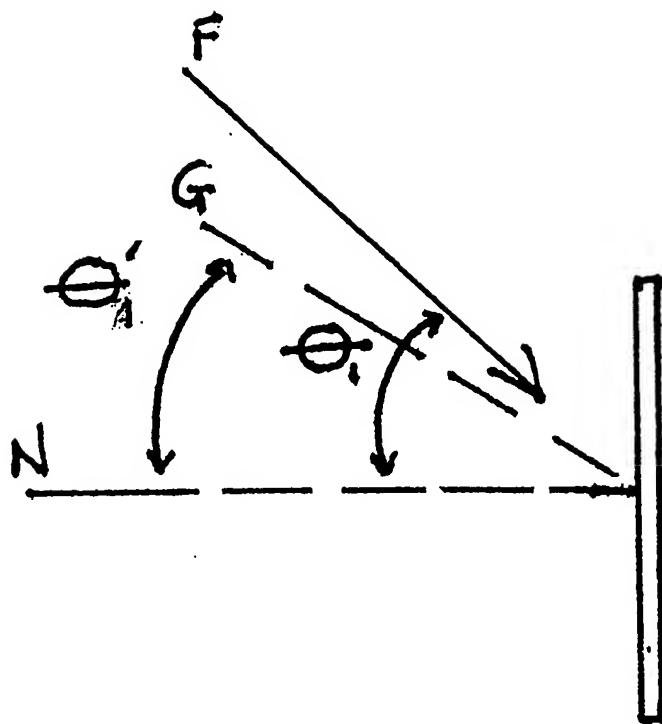


FIG. 3

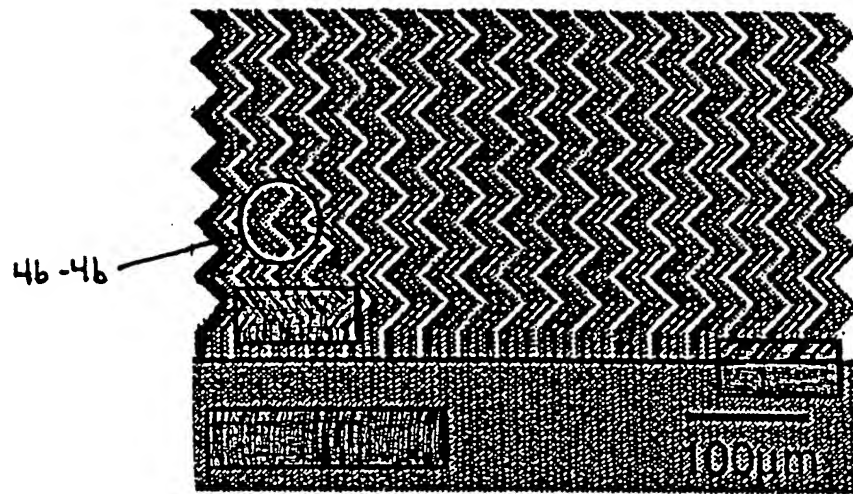


FIG. 4a

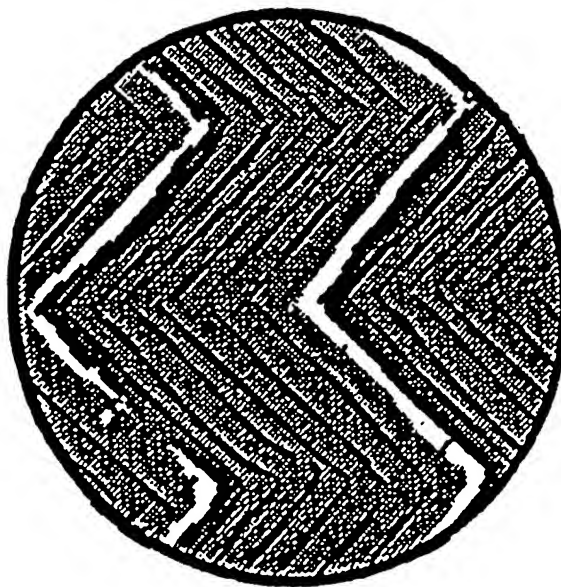


FIG. 4b

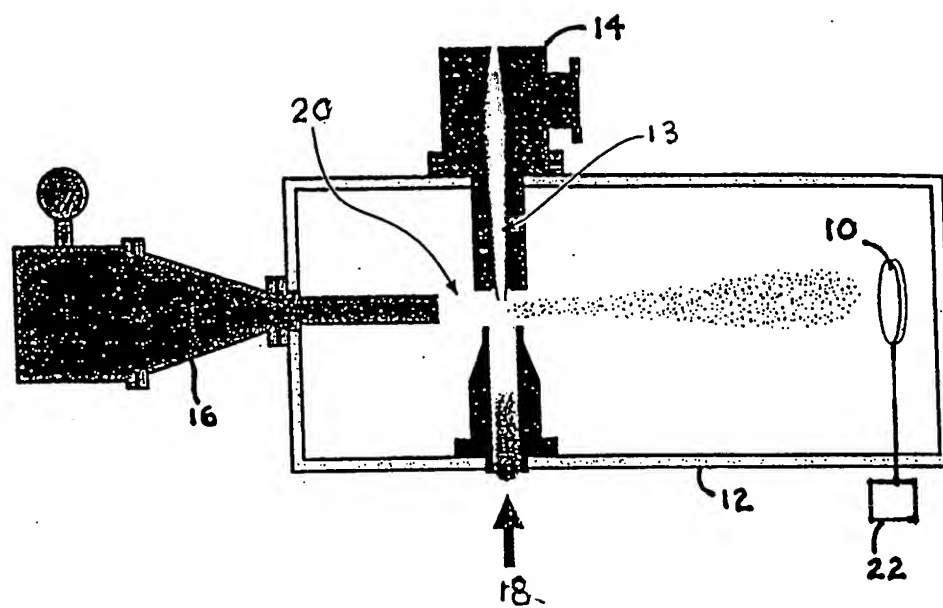


FIG. 5

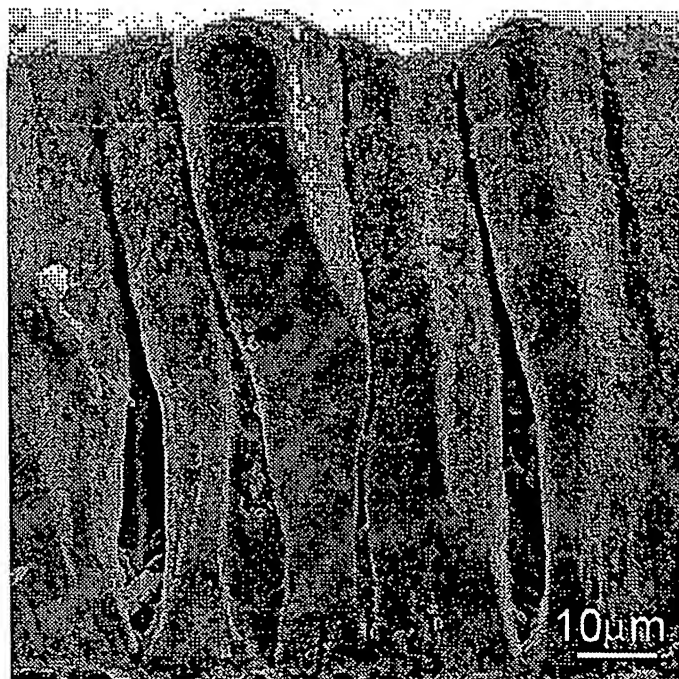


FIG. 6

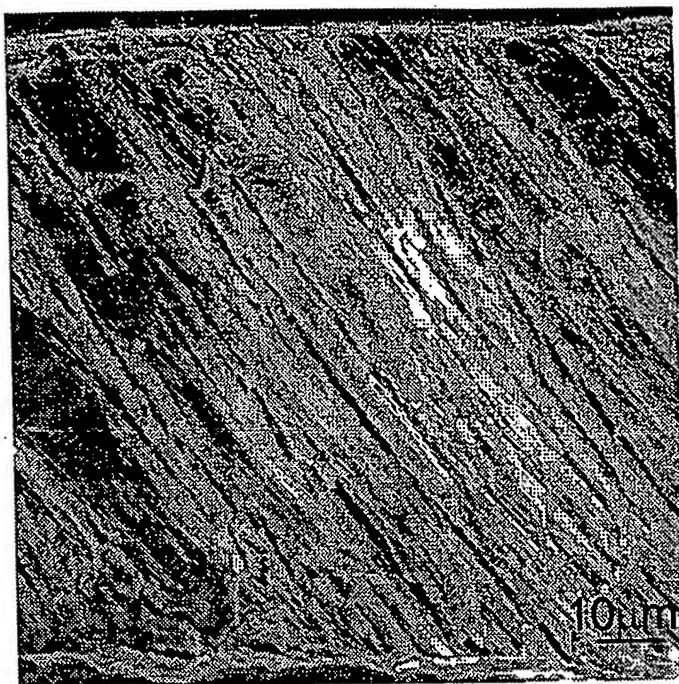


FIG. 7

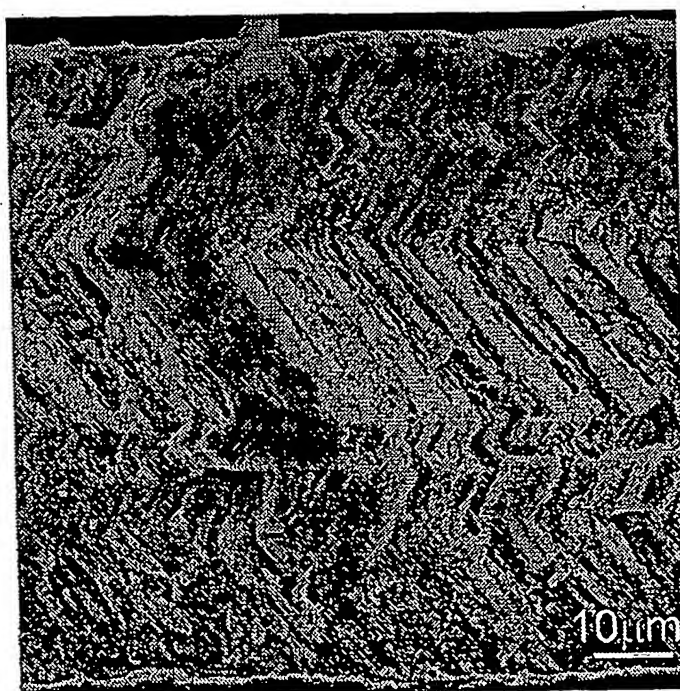


FIG. 8

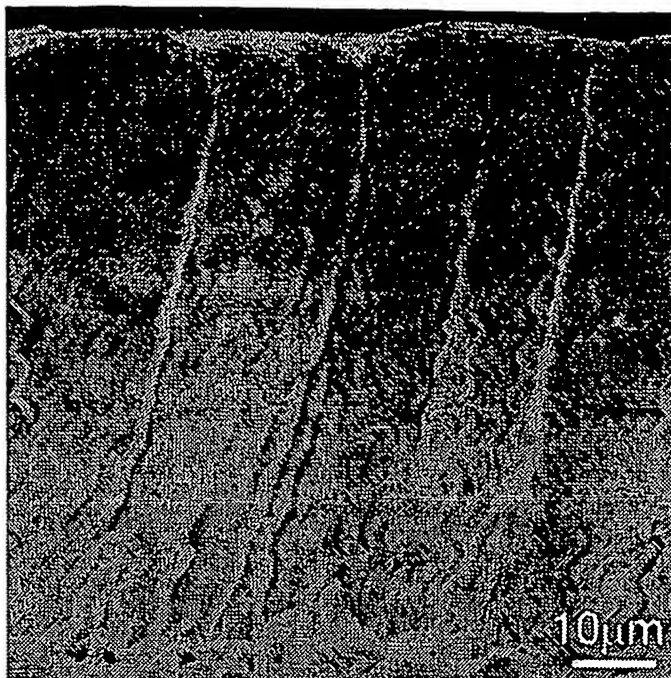


FIG. 9

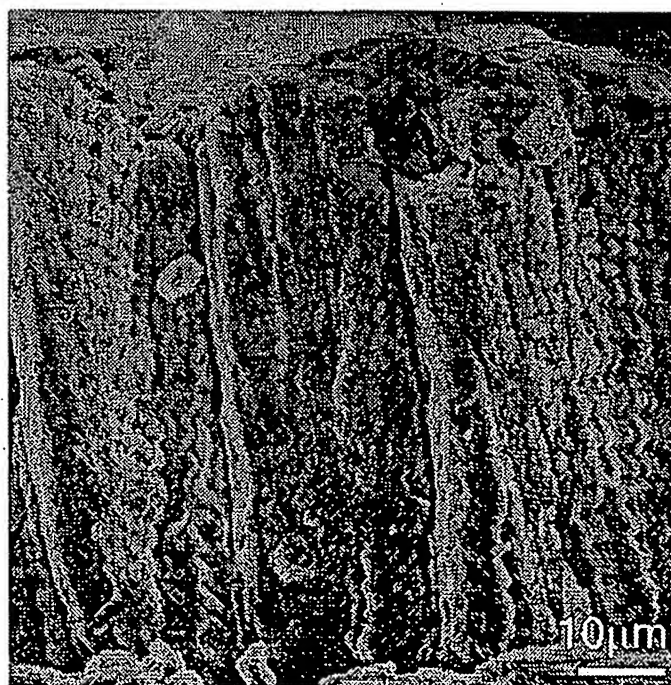


FIG. 10

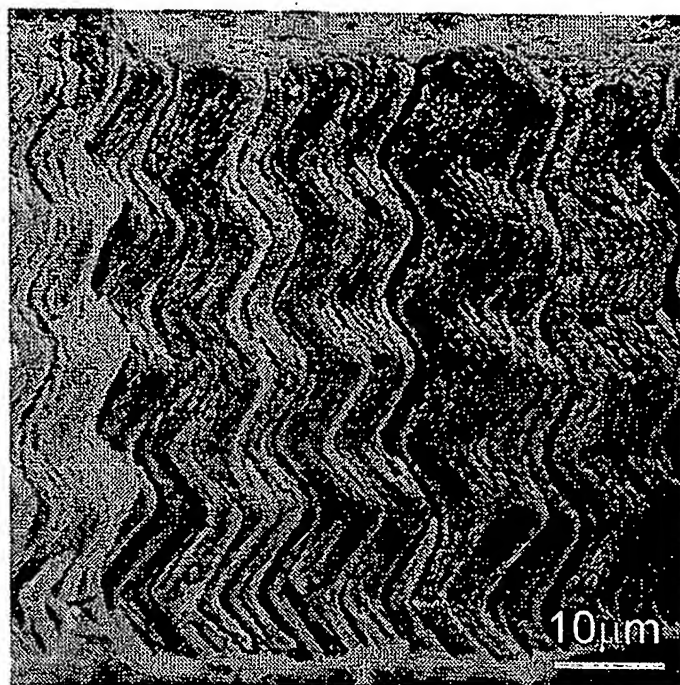


FIG. 11

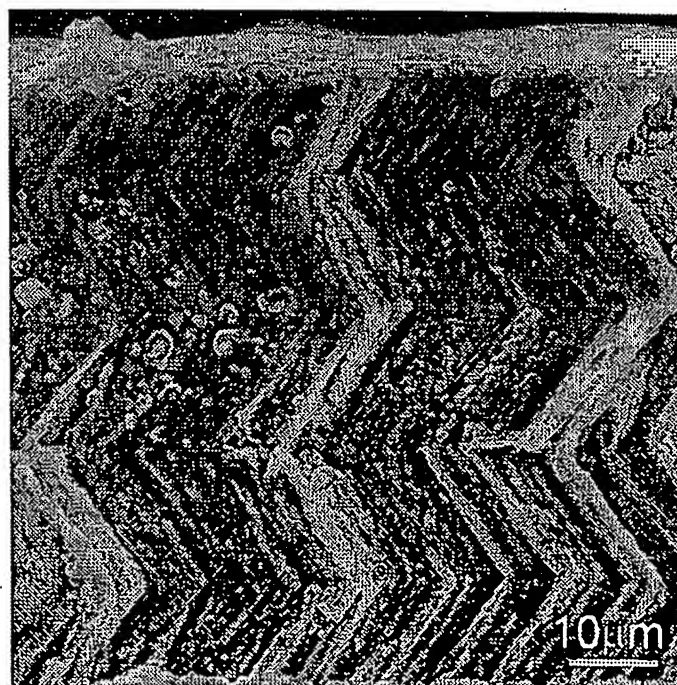


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/13450

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B21D 39/00, B05D 3/06

US CL :428/623,632,633; 427/566, 567; 118/723EB

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/623,632,633; 427/566, 567; 118/723EB

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
"APS"

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

"Thermal barrier Coating", "Top layer", "Election beam", "zig-zag"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,534,314 A (WADLEY et al), 09 July 1996 see whole document.	1-49
A	US 4,676,994 A (DEMARAY), 30 June 1987 see whole document.	47-49
A	US 4,303,694 A (BOIS), 01 December 1981.	37-46



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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